Supplementary Information for

Single molecule spectroscopic investigation on various multiporphyrin systems as a molecular photonic device

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Fig. S1 Molar extinction coefficient spectra (a) and steady-state fluorescence spectra (b) of meso-meso directly linked linear porphyrin arrays ($Z_{n+2}$).
Fig. S2 Fluorescence intensity trajectories of Z1 (a), Z2 (b), Z3 (c), and Z4 (d). The insets in (a) and (b) represent the histograms of the fluorescence intensities corresponding to each fluorescence intensity trajectory.
**Fig. S3** The STM images of **Z6** (a), **Z9** (b), and **Z48** (c). **Z6** shows a pair of images that are nearly constantly spaced at a distance of 55 Å. As bright images usually come from strong adsorption of π-conjugated molecules on a metal surface, the bright pair-based images obtained here can be assigned to the adsorption of the two end porphyrins with their planes parallel to the metal substrate. **Z9**, being similar to **Z6**, seems to take a bent conformation with the porphyrin intermediates between the two end porphyrins being detached from the metal surface. This assignment suggests conformational flexibility in the longer arrays, which is highlighted in **Z48**. The STM image of **Z48** displays a severely bent structure on the metal surface. Importantly, the molecular length of **Z48** is estimated to be 43.5 nm from this STM image, which is exactly its predicted value.
Fig. S4 Steady-state absorption spectra of Z2 and dodecameric cyclic porphyrin array C12ZA (a) and those of Z4 and tetracosameric cyclic porphyrin array C24ZB (b). The spectral red shift in the absorption spectrum of C12ZA compared to that of Z2 clearly shows the signature of strong coupling between Z2 subunits. On the other hand, the absorption spectrum of C24ZB resembles to that of Z4. The strong dipole-dipole coupling in C12ZA is believed to arise from the short interchromophoric distance between diporphyrin subunits despite weaker transition dipole strength in Z2 than that in Z4.
Fig. S5 Fluorescence intensity trajectories of 1,3-phenylene-bridged linear porphyrin array L12Z (a), cyclic arrays C12ZA (b) and C24ZB (c).
The STM images of C12ZA (a) and C24ZB (b) exhibit wheel-like structures. An average height of the STM images of C12ZA estimated on the basis of the height histogram is ca. 2.9 ± 1.2 Å and an average diameter is 35.0 ± 6.7 Å, being similar to a calculated diameter of ca. 36-38 Å. The average diameter of the STM images of C24ZB is 45-70 Å, which matches roughly with its calculated diameter (ca. 70 Å). C24ZB shows deformed images, indicating the conformational flexibility.
Fig. S7 Steady-state absorption and fluorescence spectra of cyclic porphyrin arrays C10ZA, C12ZA, C16ZA, C18ZA, C24ZA, and C32ZA in toluene. The little change in positions of the Q-bands in the absorption spectra and similar spectral shapes of the fluorescence spectra indicate that electronic coupling energies are similar for all the cyclic porphyrin arrays, which infer that angles between adjacent diporphyrin subunits are maintained approximately as 120° although cyclic porphyrin array becomes larger.
Fig. S8 Steady-state absorption spectra of zinc(II) porphyrin dendrimers (6PZnW, 12PZnW, and 24PZnW) and dendrons (1PZn and 2PZn) in chloroform (a) and spectroscopic titration spectra of 12PZnW with C₆Py₂ (0 → 300 equiv.) (b). The inset shows the absorbance change as the guest concentration increases and the fitted line as an association constant equation. The concentration of 12PZnW of 2.90 x 10⁻⁹ M and the monitoring wavelength of 419 nm were used for the titration experiments. [Py] is the total number of binding sites of C₆Py₂, which was calculated as 2 times the concentration of C₆Py₂.